Weak ferromagnetic order and possible high-T_c superconductivity in the $RuCa_2RCu_2O_{8+\delta}$ ruthenium-cuprate

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Weak ferromagnetic order with ordering temperature $T_m \sim 47$ K and possible superconducting transition with $T_c \sim 37$ K are observed for the ruthenium-cuprate $RuCa_2PrCu_2O_{8+\delta}$ with the orthorhombic distortion of the tetragonal $RuSr_2GdCu_2O_{8+\delta}$-type [with $T_m \sim 136$ K and T_c(max) ~ 65 K] phase. Anomalous temperature dependent magnetization $M_m(T)$ in both field-cooled and zero-field-cooled modes and isothermal magnetic hysteresis $M_m(B_a)$ below and above T_m and T_c indicates a very complicated coexistence and interplay between weak-ferromagnetic order and possible superconductivity. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1853274]

Recently, anomalous high-T_c superconductivity was reported in the magnetic Ru-1212 system $RuSr_2RCu_2O_{8+\delta}$ (R = Sm, Eu, Gd) with the tetragonal $TlBa_2CaCu_2O_{7+\delta}$-type (1212) structure (space group $P4/mmm$).[1–11] The occurrence of high-T_c superconductivity is closely related with the quasi-two-dimensional CuO_5 bilayers separated by rare earth in the 1212-type structure. The weak ferromagnetic or canted antiferromagnetic order observed from magnetization and neutron diffraction data with magnetic ordering temperature $T_m > T_c$ is originated from the long range order of Ru moments in the RuO_6 octahedron due to strong Ru $4d_{xy,yz,zx}$–O $2p_{x,y,z}$ hybridization.[3,4,6] In the prototype compound $RuSr_2GdCu_2O_{8+\delta}$, $T_m = 136$ K is well above the maximum reported T_c onset of 65 K.[3,11] The coexistence between superconductivity and magnetic order create many anomalous properties below T_c, which is complicated by the T_c variation with oxygen concentration parameter δ. No superconductivity was reported in the larger, isostructural compounds $RuSr_2RCu_2O_{8+\delta}$ (R = Nd, Pr).[2,7]

Through the replacement of larger Sr^{2+} ions with smaller Ca^{2+} ions, we report here the discovery of similar weak ferromagnetic order and possible superconductivity with $T_c < T_m$ in the $RuCa_2PrCu_2O_{8+\delta}$ cuprate.

The samples with nominal composition $RuCa_2PrCu_2O_{8+\delta}$ were synthesized using standard solid-state reaction. High-purity RuO_2(99.99%), $CaCO_3$(99.99%), Pr_6O_{11} and CuO (99.99%) powders were thoroughly mixed and calcined at 960 °C in air for 2 days with several intermediate regrindings. The calcined powders were then pressed into pellets and sintered at 1100 °C for 3 day in flowing O_2.

The preliminary powder x-ray diffraction analysis indicates that the crystal structure of the $RuCa_2PrCu_2O_{8+\delta}$ cuprate is a distorted orthorhombic variation of the tetragonal $RuSr_2GdCu_2O_{8+\delta}$-type structure, with orthorhombic lattice parameters $a_o \sim b_o \sim \sqrt{2}a_t \sim 0.58$ nm, $c_o \sim 2c_t \sim 2.24$ nm. However, due to the presence of small amounts of impurity phases, detailed Rietveld refinement is still in progress. However, similar RuO_6 octahedral and CuO_5 pyramidal arrangement with strong tilting relative to the c axis is expected in this distorted structure.

The temperature dependence of molar magnetization $M_m(T)$ of oxygen-annealed $RuCa_2PrCu_2O_{8+\delta}$ in 10 G field-cooled (FC) and zero-field-cooled (ZFC) mode for as-annealed sample (1) as well as for sample after 2 months (2) are shown collectively in Fig. 1. Below 47 K, sharply increasing positive magnetization indicates the onset of magnetic order with ordering temperature $T_m \sim 47$ K. At lower temperature around 37–39 K, magnetization starts to decrease and eventually becomes diamagnetic at 32 K, which is

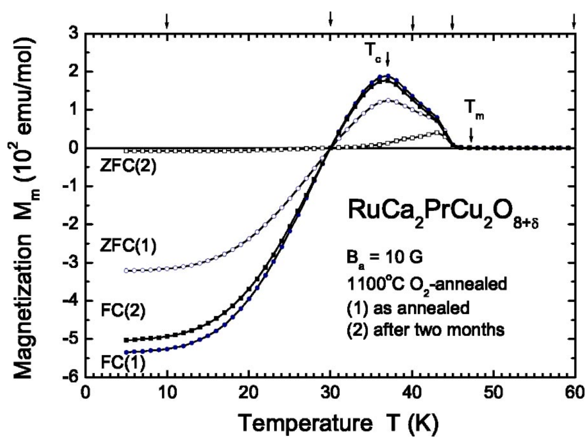

FIG. 1. Temperature dependence of molar magnetization $M_m(T)$ of oxygen-annealed $RuCa_2PrCu_2O_{8+\delta}$ in $B_a = 10$ G FC and ZFC mode for (1) as-annealed sample and (2) sample after 2 months.

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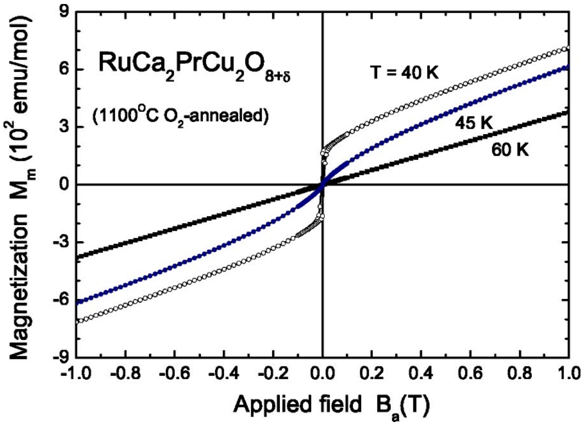

FIG. 2. Isothermal magnetic hysteresis $M_m(B_a)$ of $RuCa_2PrCu_2O_{8+\delta}$ at 40, 45, and 60 K.

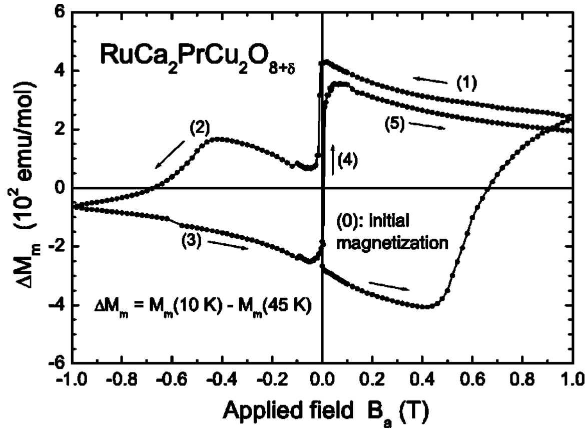

FIG. 4. Magnetization difference $\Delta M_m(B_a) \equiv M_m(10\text{ K}) - M_m(45\text{ K})$ between 10 and 45 K.

a sign of possible superconductivity with onset transition temperature $T_c \sim 37$ K. The ZFC (Meissner) diamagnetic signal is smaller than the FC (field-expulsion) diamagnetic signal. This anomalous behavior is probably due to the complex interplay between magnetic order and superconductivity below T_c. For sample measured after two months (2), smaller ZFC diamagnetic signal is probably due to sample degradation or oxygen concentration parameter δ change.

In order to check the nature of magnetic order below $T_m \sim 47$ K, isothermal magnetic hysteresis $M_m(B_a)$ at 40, 45, and 60 K are shown collectively in Fig. 2. As expected, the magnetization $M(B_a)$ at 60 K shows a simple paramagnetic straight line without any hysteresis. At 45 and 40 K, weak-ferromagnetic-like magnetic hysteresis is observed with a very small zero-field residual magnetization $M_r(0\text{ G})$ of 200 emu/mol (or 0.04 μ_B per formula unit) at 40 K, with an unsaturated magnetization of 700 emu/mol(0.13 μ_B/f.u.) up to 1 T applied field. Time-dependent magnetic relaxation $M_m(t)$ at 40 and 45 K indicates very weak relaxation.

The weak ferromagnetic order observed in $RuCa_2PrCu_2O_{8+\delta}$ is apparently originated from the long range order of Ru moments in the RuO_6 octahedron due to strong Ru $4d_{xy,yz,zx}$–O $2p_{x,y,z}$ hybridization. The Ru $4d^n$ electrons are in the t_{2g} bands due to strong RuO_6 octahedral crystal field splitting Δ_{cf} and weak Hund's rule exchange coupling J_H. The Ru self-doping with anisotropic hybridization may drive the resulting Ru^{4+}/Ru^{5+} mixed-valent system metallic and ferromagnetic via double exchange interaction. Low T_m of 47 K observed in orthorhombic $RuCa_2PrCu_2O_{8+\delta}$ as compared with 136 K observed for tetragonal $RuSr_2GdCu_2O_{8+\delta}$ indicated weaker magnetic coupling strength due to RuO_6 distortion and is very similar to the $(Ca_{1-x}Sr_x)RuO_3$ system.[12]

The low temperature isothermal magnetization at 30 and 10 K is shown in Fig. 3. Below possible superconducting transition $T_c \sim 37$ K, the hystersis curves are no longer simple ferromagnetic-like and show extremely anomalous behavior due to the complex coexistence interplay between weak ferromagnetic order and superconductivity. In order to eliminate the weak ferromagnetic contribution and dig-out a simpler behavior, the magnetization difference $\Delta M_m(B_a) = M_m(10\text{ K}) - M_m(45\text{ K})$ between 10 and 45 K is shown in Fig. 4. This gives a superconducting-like hysteris curve very similar to those observed in other high-T_c cuprates. The occurrence of possible high-T_c superconductivity is certainly closely related with the appearance of quasi-two-dimensional CuO_5 bilayers separated by Pr layer in this 1212-type struc-

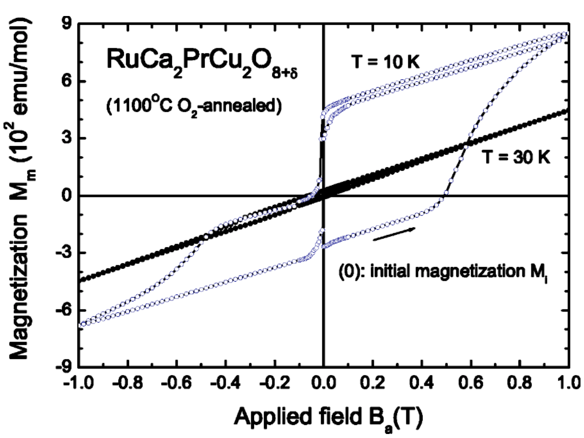

FIG. 3. Isothermal magnetic hysteresis $M_m(B_a)$ of $RuCa_2PrCu_2O_{8+\delta}$ at 10 and 30 K.

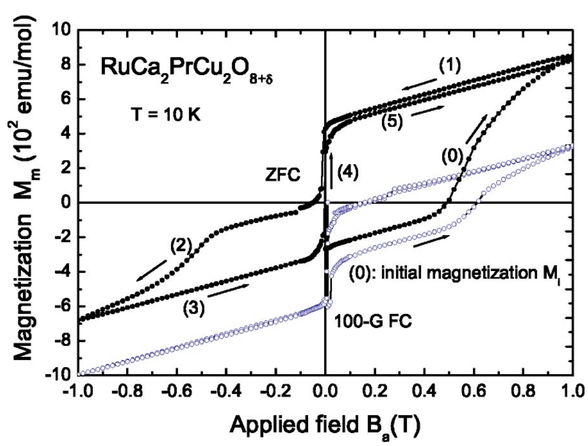

FIG. 5. Comparison of 10 K magnetic hysteresis $M_m(B_a)$ between standard ZFC mode and 100 G FC mode.

ture. However, the electrical resistivity fails to reach zero in the present investigation.

The anomalous larger FC diamagnetic signal is again due to the complex interplay. As shown in Fig. 5, the 100 G FC, 10 K isothermal hysteresis data are very similar to the ZFC data except that the whole curve has been push downward to the diamagnetic region due to some unknown reason. Detailed investigation in thus necessary and is still in progress.

In conclusion, possible superconducting onset T_c up 37 K is observed for the weak-ferromagnetic system $RuCa_2PrCu_2O_{8+\delta}$ system with $T_m \sim 47$ K. Anomalous magnetic behavior observed indicates complex interplay between superconductivity and weak-ferromagnetic order.

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